A Comparative Study of the Mineralogy and Petrology of the Mazraeh Cu-Fe Skarn Deposit, Iran and the Cu-Fe Skarn Deposit in the Edong Ore District, China

Undergraduate Research Thesis
Submitted in partial fulfillment of the requirements for graduation
with research distinction in Earth Sciences
in the undergraduate colleges of
The Ohio State University

By

Ahmad Farhan Mohd
The Ohio State University
2018

Approved by

M Barton

Dr. Michael Barton, Advisor

School of Earth Sciences

Table of Contents

ABSTRACT

Cu and Fe skarn deposits are some of the largest skarn deposits that are important for various important elements. There are exhaustive reviews of the Cu and Fe skarn deposits, but the characteristics of Cu-Fe skarn deposit are poorly explained. This thesis evaluates previous review papers concerning the Cu-Fe skarn deposits at two different geologic settings: the Mazraeh Cu-Fe skarn deposit in Iran and the Cu-Fe skarn deposit in the Edong ore district, China. These Cu-Fe skarn deposits are among the largest and most important Cu-Fe skarn deposits. Compared to Cu and Fe skarn deposits, this deposit type also consists of gold as a by-product. This thesis also summarizes the tectonic setting and petrogenesis of Cu-Fe skarn deposits and examines the petrology and mineralogy of Cu-Fe skarn deposits. This thesis focuses on studying the mineral assemblages, the ternary plots, the end-member minerals, and the thin sections of each skarn deposit for comparisons and interpretations. Prograde skarn minerals, specifically garnet and pyroxene share similar compositions in both skarn deposits. Both skarn deposits have andraditic garnet and diopsidic pyroxene. For the Mazraeh Cu-Fe skarn deposit, the endoskarn contains the red-brown andradite with composition of 45.08– 68.33 mol% andradite, 19.05–39.34 mol% grossular, and 4.52–12.33 mol% almandine. The exoskarn contains the green-yellow grossular garnet that consists of 64.25–78.88 mol% grossular, 8.77–20.55 mol% andradite, and 7.51–11.49 mol% almandine. The pyroxene is diopside-rich. The Cu-Fe skarn deposit in the Edong ore district contains 29-95 mol% andradite and 0-68 mol% grossular. The pyroxene is also diopside rich with 54-98 mol% diopside and 2-45 mol% hedenbergite. Petrological evidence shows that the prograde minerals are replaced by the retrograde minerals, including important ore minerals for Cu and Fe such as chalcopyrite, pyrite, and hematite. Both deposits have well-developed exoskarn and endoskarn system, with exoskarn containing more Cu and Fe mineralization, suggesting similar characteristics of Cu-Fe skarn deposits in the Mazraeh district, Iran and the Edong ore district, China.

Acknowledgements

First of all, I am grateful to The Almighty God for giving me strength and wisdom to write this thesis.

I would like to express my deepest appreciation to my thesis advisor, Prof. Michael Barton of the School of Earth Sciences at The Ohio State University for his enthusiasm, inspiration, and vast knowledge in the petrology and mineralogy field. His guidance and assistance had helped me enormously throughout the writing process, and I am very grateful to have him as my advisor for my undergraduate thesis.

In addition, I would like to express my sincere gratitude to Dr. Anne Carey for her continuous encouragements, insightful and constructive comments, and thought-provoking questions that significantly helped me to improve my thesis ultimately. I thank Dr. Frank Schwartz and Dr. Berry Lyons as well for their valuable feedbacks on this thesis.

I also wanted to express my special appreciation to my parents, Mohd Aripin and Siti Jahara for giving birth to me and for their exceptional and unconditional love that inspired and encouraged me to finish my thesis. I am also very thankful to my siblings, Sarah, Faiz, Firdaus, and Fakhruddin for their unceasing supports during the writing process of this thesis.

Last but not least, I also would like to thank my friends who have been through ups and downs together with me since the day I entered Ohio State as a transfer student. It has been a very difficult journey living far from home, but I am so grateful to have them in my life and to consider them as my second family, as they certainly made my undergraduate experiences in the States more memorable.

List of Figures

List of Tables

Goals and Objectives

- To study the petrogenesis and tectonic setting of skarn formation and skarn deposits.
- To examine the petrology and mineralogy of different types of skarn deposits, and compare the results with the selected Cu-Fe skarn deposits in Iran and China.
- To provide a systematic review of petrology and mineralogy of skarn deposits.
- To analyze the classification criteria of skarn and skarn deposits
- To study the skarn systems and how skarns develop over time.
- To study the similarities and differences between each skarn deposit.
- To examine the common skarn minerals such as garnet and pyroxene for different skarn deposits.
- To evaluate and make correlations between the previous articles mainly by Burt (1977) and Meinert (1992) related to each skarn deposit.
- To study various kinds of hydrothermal fluids that affect metasomatism.

INTRODUCTION

Skarn is a metasomatic rock that has been chemically altered by hydrothermal fluids from various sources, for example magmatic fluids flowing into carbonate rocks, e.g., limestone and dolostone. Skarn is comprised of calc-silicate minerals, such as garnet, epidote, pyroxene, and wollastonite. Skarn that contains important economic minerals is commonly referred to as a skarn deposit. These can be classified and named according to the particular element that are mined. Skarn deposits are known to be sources of Fe, Cu, W, Au, Zn, Sn, and Mo. Fe skarn deposits are the most abundant and largest of these, followed by Cu types.

Due to their complex nature, skarn remain of interest to geologists all over the world. Significant progresses are have been made towards understanding the skarn systems and improving the classification terms for these. Yet, skarn deposits that contain more than one type of economic mineral are still difficult to interpret and classify. Cu-Fe skarn deposits, which are the focus of my work are good examples.

Accordingly, this thesis focuses on the classification of Cu-Fe skarn deposits by comparing the similarities and differences between Cu-Fe skarn deposits in the Mazraeh district, Iran, and those of the Edong ore district, China. The comparisons of Cu-Fe skarn deposits with other Cu and Fe skarn deposits in the adjacent areas are also mentioned based on the mineralogy and petrology of each skarn deposit. The hypothesis of this study is that the similarities outweigh the differences in the Cu-Fe skarn deposits in Iran and China as well as of those deposits in adjacent areas. I also examine how similar the garnet and pyroxene minerals are in the indicated Cu-Fe skarn deposits. These are indicated to be andradite and diopside, respectively based on the review by Meinert (1992).

The Mazraeh Cu-Fe skarn deposit was chosen for this study because it is the most common type of skarn deposits in NW Iran. This particular deposit is situated about 5 km N of the village of Mazraeh. It is formed due to the intrusion of granitic rocks of Oligo-Miocene age into carbonate rocks. Based on the petrological analysis, this skarn deposit has been subdivided into three zones: endoskarn, exoskarn, and ore skarn. The major skarn minerals in this deposit are garnet and pyroxene as well as typical Cu and Fe ore minerals, such as chalcopyrite, hematite, and pyrite (Karimzadeh Somarin, 2010).

The Cu-Fe skarn deposit in the Edong ore district, China is one of the many deposits found in this district and one of the largest in China with estimated of Fe and Cu reserves of 99% and 57% respectively (Xie *at al.*, 2015). Several papers have already discussed the characteristics of Fe and Cu-Fe skarn deposits in this district. However, this thesis aims to make detailed comparisons of Cu-Fe skarn deposits in the Mazraeh district and the Edong ore district based on mineralogy and petrology. The results will specifically examine between these deposits.

An Overview of Skarns and Skarn Deposits

Skarn Formation

Skarn is an old Swedish term that refers to the gangue minerals that are associated with sulfide deposits and Precambrian magnetite (Burt, 1977). Usually, skarn is classified as a metamorphic rock because it forms during contact and regional metamorphism, accompanied by metasomatism. Metasomatism refers generally to chemical and mineralogical alteration due to circulating hydrothermal fluids. This process results in recrystallization and compositional variations in the rocks.

Hydrothermal fluids are naturally heated and contain various dissolved elements and gases. Magmatic fluids are also called juvenile waters. They occur within and in equilibrium with the magma or the volatile fluids associated with magma. Magmatic fluid is usually released during a volcanic eruption to the atmosphere. Fluid that is derived from precipitation, e.g., snow and rain and that accumulates in oceans, lakes, rivers, and ice melt is known as meteoric. Metamorphic fluid is the fluid that saturates the pore space (primary and secondary) in metamorphic rocks. It is important because of the dissolved constituents. This kind of fluid is also produced by the dehydration hydrous minerals during metamorphism. Fluid that is derived from oceans and modified geochemically through thermal interactions with the Earth's crust is referred to as marine.

Several studies support Burt's (1977) idea that skarn is a metasomatic rock formed by alteration of a metamorphic rock (Meinert, 1992, 1993; Dyer *et al.*, 2011). Metamorphic rock is considered to be formed due to processes that change the mineral assemblages within the rock itself. These processes are driven by changes in temperature and pressure that facilitate the development of metamorphic rocks over time. However, metasomatic rock is considered to be formed by process that create changes in rock minerals by the importation of elements from external sources. The most common case with skarn are processes related to igneous intrusions into host rocks.

Skarns are commonly associated with carbonate rocks, such as limestone, dolostone, and marble (metamorphosed carbonate rock). However, they can form in any type of rock, including shale, granite, and basalt. A typical conceptual model includes a pluton associated with host rocks, usually carbonate rocks or sedimentary rocks, with the skarns created by wall-rock interactions by metasomatic processes. In addition, skarns can be found along major shear zones and major faulting zones that provide suitable conditions for their formation. Complexity also comes from the fact that skarns can continuously change their mineral assemblages over time as suitable conditions develop conducive to the formation of specific minerals. There is typically a progression from prograde to retrograde skarn minerals (Burt, 1977).

Skarn Mineralogy and Petrology

Skarns are defined by their minerals. Typically, these include various calc-silicate minerals such as diopside, epidote, and wollastonite. However, garnet and pyroxene usually dominate, regardless of the skarn type. Skarn mineralogy is classified based on the grade of alterations, which is represented by the prograde and retrograde minerals.

Prograde minerals reflect changes in mineral assemblages, which come from heating and burial processes that lead to increases in temperature and pressure. Examples of important prograde skarn minerals include intermediate garnet -grossularite to andradite, diopsidic pyroxene, magnetite, wollastonite, and epidote.

Retrograde minerals reflect mineralogic changes occurring due to cooling and uplift processes that produce decreases in temperature and pressure. At this stage, anhydrous minerals are replaced by hydrous minerals able to form at relatively lower temperatures. Several important retrograde skarn minerals are amphibole, chlorite, epidote, and various other hydrous minerals. Retrograde mineralization commonly leads to overprinting of the zonation sequences and textures associated with the prograde minerals, e.g., garnet and pyroxene, and may be associated with vein structures (Einaudi and Burt, 1982). However, replacement of hydrous minerals does not necessarily represent retrograde alteration, as there are other factors that may be relevant in some cases, such as the fluorine and carbonate activities (Dick and Hodgson, 1982). Retrograde alterations also might completely eliminate the previously formed prograde minerals from the skarn. This more intense alteration makes rock interpretations more difficult (Einaudi and Burt, 1982).

Garnets are essential in determining the differences in the mineralogy of skarn deposits (Figure 1) because they are present in almost all skarn deposits, they are stable (high resistance to weathering), and typically occur as relatively large crystals, about a few centimeters in diameter (Karimzadeh Somarin, 2004, 2010). These characteristics make sampling and mineralogical assessments easier. Garnet is also a refractory mineral, which can preserve the history of the process of skarn formation, and also the trace element contents for various specialized studies, e.g., mineralogy and petrology (Jamtveit, 1991; Putnis, 2002; Gaspar *et al.*, 2008). The general formula of garnet is $X_3Y_2(SiO_4)_3$. The classification and end-member of garnet is listed below in Table 1:

Table 1: The classification and end-member of garnet. Modified from Meinert (1992).

Pyralspite garnets: Contain aluminium in Y site.	Ugrandite garnets: Contain calcium in X site.
Almandine: $Fe_3Al_2(SiO_4)_3$	Andradite: $Ca_3Fe_2(SiO_4)_3$
Pyrope: $Mg_3Al_2(SiO_4)_3$	Grossular: $Ca_3Al_2(SiO_4)_3$
Spessartine: $Mn_3Al_2(SiO_4)_3$	Uvarovite: $Ca_3Cr_2(SiO_4)_3$

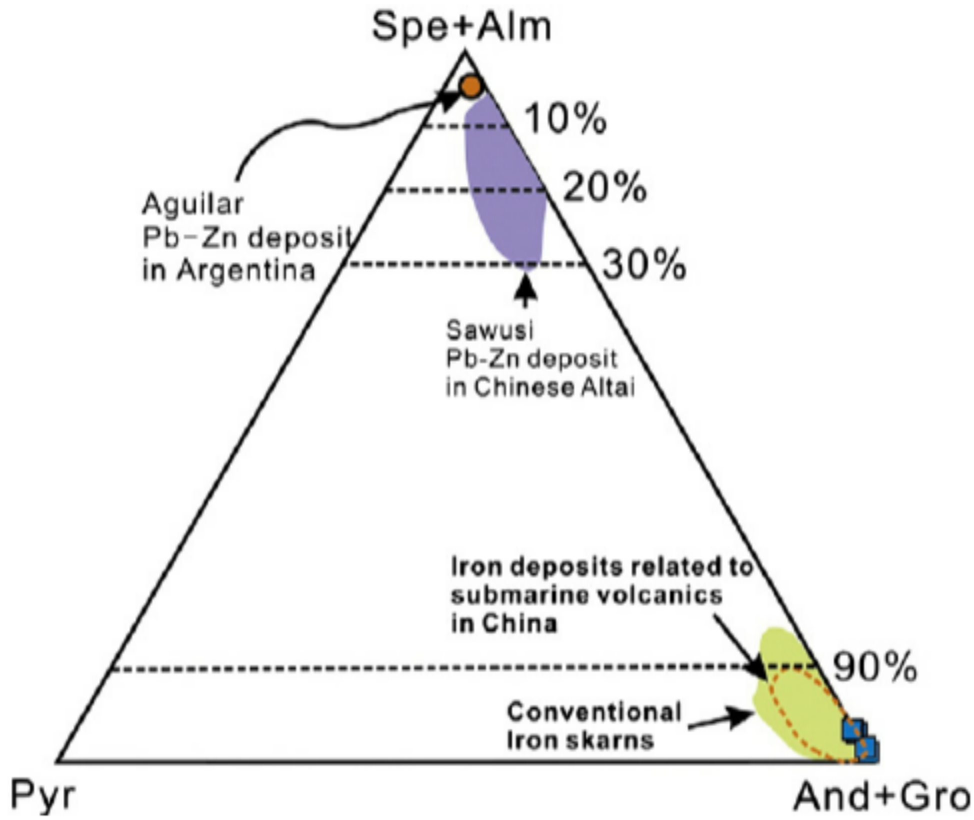

Figure 1: The triangular plots of garnet composition. The figure includes data related to Fe skarn deposits and other deposits from different source, specifically from submarine volcanic rocks. And+Gro is also known as grandite. Spe: Spessartine, Alm: Almandine, Pyr: Pyrope, And: Andradite, and Gro: Grossular. Taken from Hou *et al.* (2014).

The term pyroxene refers to a group of rock-forming silicate minerals. Pyroxene is very important in skarn formation and skarn deposits because it is found in associated igneous rocks and can occur with a wide range of mineral composition under conditions prevailing during regional and contact metamorphism. Some examples of pyroxenes in different types of skarn deposits are diopside and hedenbergite (Fe-rich) (Figure 2).

Similar to pyroxene, feldspar is another group of rock-forming silicate minerals, which occur in igneous rocks and metamorphic rocks. Feldspar is subdivided into the alkali feldspar (K-rich) and plagioclase feldspar (K-poor) classes. The end-member of plagioclase feldspar is albite, with sodium as the Na end-member, and anorthite, as the calcium end-member (Figure 2). These end-members are important for understanding the mineralogy of various types of skarn deposits.

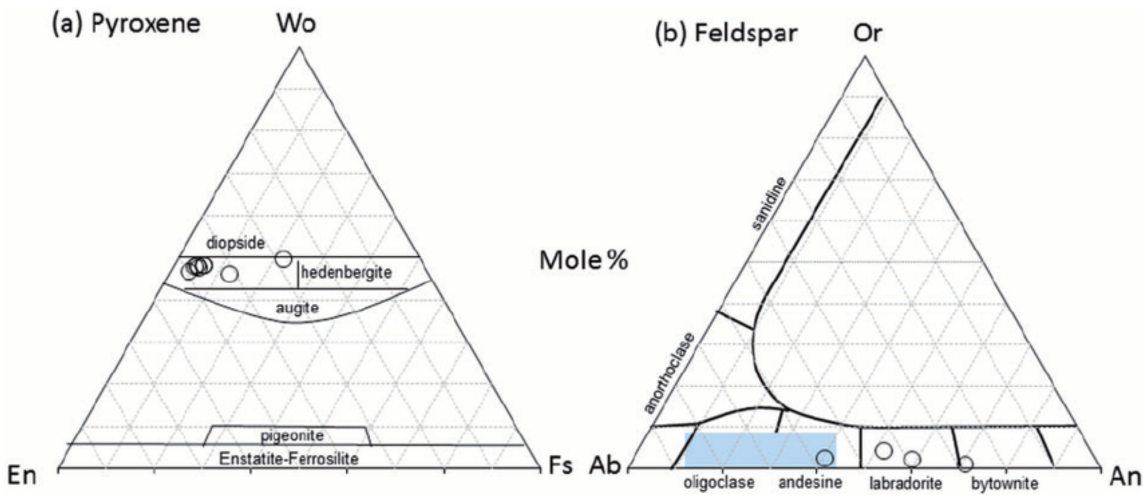

Figure 2: Triangular plots for pyroxene and feldspar. Wo: Wollastonite, En: Enstatite, Fs: Ferrosilite, Or: Orthoclase, Ab: Albite, and An: Anorthite. Taken from Dyer *et al.* (2011).

Skarn Classification

This thesis focuses on providing an understanding of the characteristics of skarn deposits, which are skarns that contain ore minerals. Skarn deposits are typically classified based on the protolith, the distance of the deposits from the heat source (e.g., a pluton), and the important economic elements mined from the deposits.

Based on the proximity to the heat source:

Exoskarn– The protolith is of sedimentary rock. An exoskarn usually forms away from an intrusion due to the interactions of wall-rock and pluton, which create alteration in the wall-rocks (Meinert, 1992; Dyer *et al.*, 2011).

Endoskarn– The protolith is of igneous rock. An endoskarn usually forms within the rock-mass itself, and is associated with the alterations of igneous rocks with widespread albite and the stockworks due to cooling processes of veins and joints (Meinert, 1992; Dyer *et al.*, 2011).

A study by Dyer *et al.* (2011) pointed out that exoskarns and endoskarns can occur in the same system. They are differentiated based on their mineralogy and the distance away from the heat source. Differences in mineralogy develop as a consequence of the particular conditions that develop at different places, which control the replacement and recrystallization of certain minerals and elements. Based on Figure 1, the plagioclase content decreases and the pyroxene content increases farther away from the pluton (Dyer *et al.*, 2011). The changes are due to the fact that plagioclase is being replaced by pyroxene. For example, the endoskarn forms in association with the igneous rock, which might be granodiorite, and exoskarn forms in association with marble, which is a metamorphosed limestone (Figure 3).

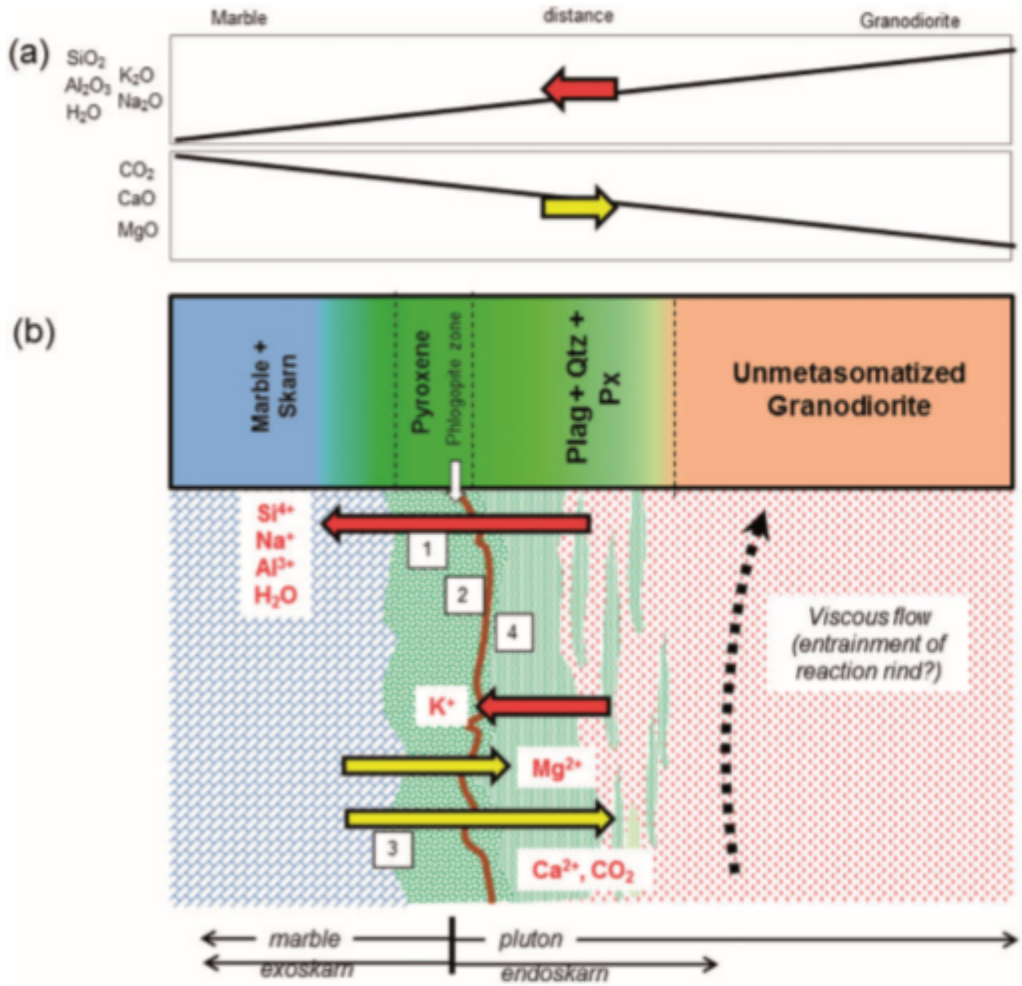

Figure 3: Formation of exoskarn and endoskarn due to the wallrocks-pluton interactions that produce the various alterations in mineralogy. Endoskarn forms closer to the pluton compared to exoskarn. Endoskarn forms in the vicinity of the igneous rock of the pluton, and exoskarrn forms in the marble. The red arrow shows the chemical gradient or movement of ions and chemical compounds from the granodiorite towards the marble. The yellow arrow shows the movement of ions from marble towards the granodiorite. Modified from Dyer *et al.* (2011).

As mentioned, skarn deposits are also classified on the basis of their economic mineral content Table 2). There are several important elements mined from ore-bearing skarns, such as iron, tungsten, gold, copper, zinc, molybdenum, and tin (Meinert, 1992). In certain cases, skarn deposits may contain more than one valuable element. The nomenclature for classifying deposits would start by naming the element with the lowest percent abundance and end with the element with the largest percentage abundance (Meinert, 1992). For instance, skarn deposits that contain Au and Cu, where the percentage of Au is higher than Cu, would be classified as Cu-Au skarn deposits. Some distinct characteristics, including the mineral assemblages and the economic importance for each skarn type are described below:

Iron-rich skarn deposits—These deposits represent the largest skarns (Meinert, 1992, 1993). This type of skarn deposit is discussed extensively in review papers by Sangster (1969), and Einaudi *et al.* (1981). Iron skarn deposits are subdivided into two main categories depending on the protolith or host rock comprised of limestone or dolostone. Contact with some adjacent pluton that provides iron-rich source minerals are transported by way of hydrothermal fluids. Skarn deposits that are formed due to hydrothermal alteration in the limestone are called calcic iron skarn deposits. These are typically associated with oceanic island arcs. The iron-rich minerals in this type of deposit are primarily iron-rich forms such as garnet and pyroxene, and contain minor occurrences of actinolite, ilvaite, and epidote (Purtov *et al.*, 1989). Meanwhile, skarn deposits that are associated with dolostone are called magnesian iron skarn deposits. These commonly form in dolomitic wall rocks. The minerals consist of iron-poor minerals, such as the end-members of olivine (forsterite and diopside), talc, serpentine, and periclase (Hall *et al.*, 1988).

Iron ore deposits are important economically for the production of iron and steel. This raw material is important for industries like automobiles and construction.

Tungsten-rich skarn deposits—Typically, such deposits are found on continents, where they are associated with calc-alkaline plutons in orogenic belts. Review papers that focus on these types of skarn deposit are Newberry and Einaudi (1981) and Newberry (1998). Tungsten skarn deposits occur together with equigranular and coarse-grained batholiths enclosed by high temperature metamorphic aureoles. These aureoles contain abundant calc-silicate hornfels typically that produce a distinct texture useful in petrological analysis. Tungsten skarn deposits are further classified into two main categories which are reduced type and oxidized type and their differences in the host rock composition (hematitic versus carbonaceous) and the skarn mineralogy (Fe^{2+} versus Fe^{3+}) (Newberry and Einaudi, 1981).

Reduced type skarn deposits contain in abundance the garnet (grandite), pyroxene (hedenbergitic) and molybdenum-rich scheelite. This latter mineral is valuable for tungsten it contains. A study by Newberry (1983) suggests that the garnet is subcalcic, ranging from spessartine to almandine due to the leaching of dispersed scheelite and the redeposition of molybdenum-poor scheelite. These tungsten skarns also contain sulphide minerals, such as molybdenite, sphalerite, and pyrrhotite, and hydrous minerals, such as hornblende, biotite, and epidote. A study by Soloviev and Kryazhev (2018) of the tungsten skarns in the Tien Shan Gold Belt, found the garnet composition to be dominated by grossular garnet with abundant grandite and pyroxenes comprised of hedenbergite, which is indicate of a reducing environment.

The oxidized type of deposit has more garnet (andraditic) as compared to pyroxene, with molybdenum-poor scheelite. Compared to the reduced type, this type contains more ferric iron than ferrous iron, and tends to be smaller in size than the reduced tungsten skarn (Newberry, 1983). Tungsten is important economically because of its relatively high melting point as compared to other metals found on Earth. It is usually alloyed with other metals to strengthen them in high-temperature applications. Tungsten is also mainly used for light bulb filaments due to its high melting point, and is also finds important applications in drilling equipment in the mining and petroleum industries.

Gold-rich skarn deposits—The gold produced from these skarns is typically a by-product from the mining of copper. This type of skarn deposit came into play due to the extremely high price of gold in the early 1970s. Examples of this skarn deposit include the Nickel Plate mine in the Hedley district, British Columbia (Billingsley and Hume, 1941), the Crown Jewel deposit, Washington (Hickey, 1990, 1992), and the Fortitude deposit, Battle Mountain District, Nevada (Kotlyar and Theodore, 1998). Review papers that examine this type of skarn deposit in detail are Ettlinger (1990), Ettlinger and Ray (1993), Ray *et al.* (1987, 1988), and Dawson and Ray (1994). Similar to other skarn deposits, gold skarn deposits are exploited mainly for the gold. However, a skarn deposit that has a relatively high amount of gold is not necessarily called a gold-rich skarn deposit. The classification in these cases depend on other economic materials associated with the deposit. A good example is the Big Gossan deposit (Meinert *et al.*, 1997). Normally, gold skarn deposits have low ratio of garnet to pyroxene, have hedenbergitic pyroxene, and have abundant sulphides, for instance pyrrhotite and arsenopyrite (Brooks *et al.*, 1991).

The reduced gold skarn deposit is the most important type of gold skarn deposit, and yields the highest grade, thereby maximizing the skarn's economic value based on the gold mined. This reduced type is usually associated with reduced diorite-granodiorite plutons and dike-sill complexes (Meinert *et al.*, 1997). This type tends to form in clastic-rich protoliths, as compared to pure limestone or dolostone. The minerals in this type of deposit consist of hedenbergite, grossular and andradite in the proximal zones with some other common minerals such as alkali feldspar, amphibole, and apatite.

Gold is a very important and useful metal for many industries, which are summarized below:

- Jewelry: Gold has distinctive properties that makes it very desirable, such as resistance to tarnishing, a beautiful lustre, and malleability. Gold is also alloyed with other metals such as silver or copper to increase its durability and provide variations in color, although the alloys are not as valuable as pure gold.
- Electronics and Computers: Gold is an efficient conductor, because it is able to conduct electric currents without being affected by tarnish or corrosion. Commonly, gold is alloyed with cobalt or nickel to increase its durability.
- Aerospace: Gold is used also used in this industry for circuitry. Gold also finds application in polyester film coatings for rockets and other space vehicles. It helps to reflect infrared radiation and to stabilize the temperature in those vehicles. Gold is also useful as a lubricant, because it does not volatilize in vacuum, as compared to other organic lubricants. Its ability to function as a lubricant comes from its low shear strength that reduces friction forces.
- Medical: A major use of gold in medicine is with radioactive gold available for diagnostic purposes. Gold is non-reactive when used in medical instruments, for instance surgical instruments, and life-support devices.

Copper-rich skarn deposits—These are also considered among the largest skarn deposits, along with iron-rich skarn deposits. This type of deposit is commonly found in places with a variety of different tectonic settings, for example, orogenic zones and belts in areas of subduction in continental or ocean tectonic settings (Meinert, 1992). Papers that review this type of skarn include Einaudi *et al.* (1981) and Einaudi and Burt (1982). This deposit type is associated with relatively shallow environments, where the deposit consists of minerals that are from the magnetite series, and calc-alkaline (Einaudi and Burt, 1982). This type is also primarily associated with porphyritic plutons, stockwork veining, intense hydrothermal alteration, and brittle fracturing (Einaudi and Burt, 1982). Minerals associated with this type of skarn include andraditic (Fe-rich) garnet, diopsidic pyroxene, and other distinct minerals, for instance actinolite, wollastonite, and epidote (Einaudi and Burt, 1982). Based on a study by Karimzadeh

Somarin (2004), the composition of andraditic garnet in copper-rich skarn deposits is very useful in determining the likelihood of copper mineralization because it has higher copper concentration than for example copper-poor deposits due to the replacement of iron by copper.

With deposits that reflect interaction between wall rocks and dolomitic host rocks, the minerals found are magnetite and hematite. These are important ore minerals for iron. If the host rocks are marble, copper skarn deposits are typically zoned with garnetite adjacent to the plutons to pyroxene and then to wollastonite or idocrase moving away from the pluton (Einaudi *et al.*, 1981). Copper is a commonly-used metal for coin productions alongside gold and silver. It is also used for electric wiring and in motors because copper is a good electrical and heat conductor.

Zinc-rich skarn deposits—This type of skarn deposit normally forms due to processes of rifting or subduction in continental settings. These deposits are typically high grade in terms of dominant ores of zinc, silver, and lead. They form as shallow dike-sill complexes, deep sea batholiths, and surface volcanic extrusions (Einaudi *et al.*, 1981). These types of skarn are different from others because of an iron and manganese-rich mineralogy, and because they form adjacent to the lithological contact, and the absence of metamorphic aureoles at the center of the skarn formation. The minerals found are typically rich in manganese, including garnet, pyroxene, amphibole, olivine, chlorite, and serpentine. Detailed reviews of this skarn deposit are found in Einaudi *et al.* (1981) and Megaw *et al.* (1988). Zinc skarn deposits are classified based on the criteria listed below:

- Percentage of skarn and sulphide minerals.
- Formation temperature, and
- Distance from the magmatic source

However, based on the review by Megaw *et al.* (1988, 1998), these criteria are somewhat superficial and insufficient for detailed interpretation. Most skarn deposits contain both skarn-rich and skarn-poor ores, hence making the percentage calculation to be incorrect. Besides, skarn deposits can develop over a wide range of temperature, and the mineralogical assemblages can change depending on the prograde or retrograde conditions. Lastly, magma source for some deposits could not be identified due to complex geological and tectonic settings (Megaw *et al.*, 1998). Further study by Megaw *et al.* (1998) suggests that most zinc skarn deposits behave similarly, in which the mineralization changes from skarn-rich to skarn-poor ores outwards from the magmatic source.

Molybdenum-rich skarn deposits—These deposits are associated with high to low grade leucocratic granites (Einaudi *et al.*, 1981). This type of skarn deposit normally forms in carbonate or calcareous clastic rocks. An example is the deposit at Cannivan Gulch, Montana (Darling, 1990). There have not been no recent reviews after the summary by Einaudi *et al.* (1981). This type of deposit can contain various important elements but in limited quantities such as lead, zinc, copper, and tungsten. However, this deposit type is polymetallic, where multiple elements need to be recovered together to make the deposit economic. The most common type is molybdenum-tungsten-copper deposit, and some tungsten or copper skarn deposits may contain zones of molybdenum. Minerals found in this deposit include hedenbergitic pyroxene with lesser grandite garnet, and some other important minerals, for instance amphibole, wollastonite, and fluorite (Einaudi *et al.*, 1981). The mineralogy, featuring high fluorine activities indicates that this deposit behaves in a reducing environment. Some economic uses of molybdenum are:

- Alloy productions to make steel stronger,
- For electrodes in glass furnace because it has high melting point similar to tungsten. and
- For catalysing the removal of organic sulfur in the gas liquification and coal liquification in the petroleum industry.

Tin-rich skarn deposits—These deposits are associated with high-silica granites formed by partial melting of continental crust (Einaudi *et al.*, 1981). Most tin skarn deposits are spatially zoned from skarn-rich to skarn-poor. This deposit type has distinct mineralogical characteristics, in which tin is typically found together with unrecoverable silicate minerals economically, such as garnet, idocrase, and sphene (Dobson, 1982; Kwak, 1987). Some review papers that discuss this particular deposit are Einaudi *et al.* (1981) and Kwak (1987). Tin skarn deposits can be categorized based on important comparisons listed below:

- Calcic (limestone host rock) versus magnesian (dolostone host rock),
- Skarn-rich versus skarn-poor minerals,
- Oxide-rich versus sulphide-rich minerals,
- Proximal versus distal (related to the heat source), and
- Greisen versus skarn

Based on the review by Eunaidi *et al.* (1981), this deposit type is also linked with suites of other trace elements in the ores and the igneous rocks. This feature makes this skarn deposit distinct from other skarn deposits based on the major element mined. A subsequent study by Kwak (1987) claims that tin skarn deposits are associated with greisen alteration, which is characterized by high fluorine activities and also the presence of distinctive minerals, such as fluorite, quartz, tourmaline, muscovite, and ilmenite. The greisen alteration might superimpose the hydrothermal fluid intrusion, which is a distinct feature of tin skarn deposits. Kwak (1987) also suggested that the skarn deposit of interest is the distal part of the deposit, in which more oxide and sulphide replacements occur without the loss of tin element in the calc-silicate minerals. Tin is economically important for various purposes. Some major uses are for the metal coating, such as tin cans to prevent corrosion. Tin is used for alloy production with niobium for the superconducting magnet production.

Table 2: The simplified and summarized version of the type of garnet and pyroxene for skarn deposits classified based on the important economic elements. Data were obtained from Einaudi and Burt (1982) and Meinert (1992). Further interpretations are needed to get a consensus on the type of garnet and pyroxene for tin-rich skarn deposit.

Type of skarn deposits based on economic element	Type of garnet	Type of pyroxene
Iron	Andradite	Calcic - Hedenbergite Magnesian – Diopside
Tungsten	Reduced - Grandite Oxidized - Andradite	Hedenbergite
Gold	Grandite	Hedenbergite
Copper	Andradite	Diopside
Zinc	Spessartine	Hedenbergite
Molybdenum	Grandite	Hedenbergite
Tin	Uncertain	Uncertain

GEOLOGIC SETTINGS

Mazraeh Cu-Fe Skarn Deposit, Iran

The Mazraeh skarn deposit contains relatively high amount of Cu-Fe skarn deposit with about 400,000 tons sulphide reserve of 1.2% Cu grade (Karimzadeh Somarin 2005, 2006). Skarn deposits in the NW Iran are classified into two major groups; the Cu-rich and the Cu-poor (Karimzadeh Somarin, 2010). Mazraeh skarn deposit is the Cu-rich type. This deposit is located in the Cu metallogenic zone of Ahar in the northwestern (NW) Iran of the Alborz-Azarbaijan geotectonic zone, which was considered as one of the most magmatically active zones in Iran (Karimzadeh Somarin 2005, 2006). This deposit also is located in the Alpine-Eurasian metallogenic belt that spreads from Greece towards Iran. The Cu-Fe deposit is associated with the I-type granitic plutons of the magmatic belt with the trend of NW-SE. Most of these plutons were formed during Oligocene-Miocene magmatism events, and emplaced during the Pyrenean Orogeny (Karimzadeh Somarin, 2006). Then, submarine volcanism events during the Eocene age deposited high amount of andesitic to dacitic volcanic rocks (Karimzadeh Somarin, 2005). Successive volcanic events during the Eocene-Oligocene period in Azarbaijan produced calc-alkaline and locally alkaline volcanic rocks that cover most parts of the NW Iran. Crystal fractionations and assimilations occurred periodically and controlled the chemistry of the volcanic rocks that were produced in a continental margin of the volcanic arc environment.

The ore deposits of the Ahar region are associated with the Oligocene-Miocene granitic plutons and then intruded into the Oligocene acid-intermediate volcanic rocks, the Cretaceous limestones, and the Eocene terrigenous sedimentary rocks (Fig. 4). These types of mineralization are dependent on the geology and composition of the country rocks, and the composition and depth of the pluton emplacement (Meinert 1992; Meinert et al. 2005).

The Mazraeh granodiorite ranges from light to dark gray with the hypidiomorphic texture. The groundmass is typically medium to coarse-grained and composed of plagioclase, quartz, K-feldspar, and hornblende. The phenocrysts are plagioclase and K-feldspar. The accessory minerals are apatite, biotite, magnetite, and titanite. The Mazraeh plutons consist of monzonite to quartz monzonite, monzogranite, granodiorite, and tonalite (Fig. 5).The composition varies from medium to high K calc-alkaline containing 1.82–4.78 wt.% K_2O and 57.22–70.49 wt.% SiO_2 (Fig. 6).

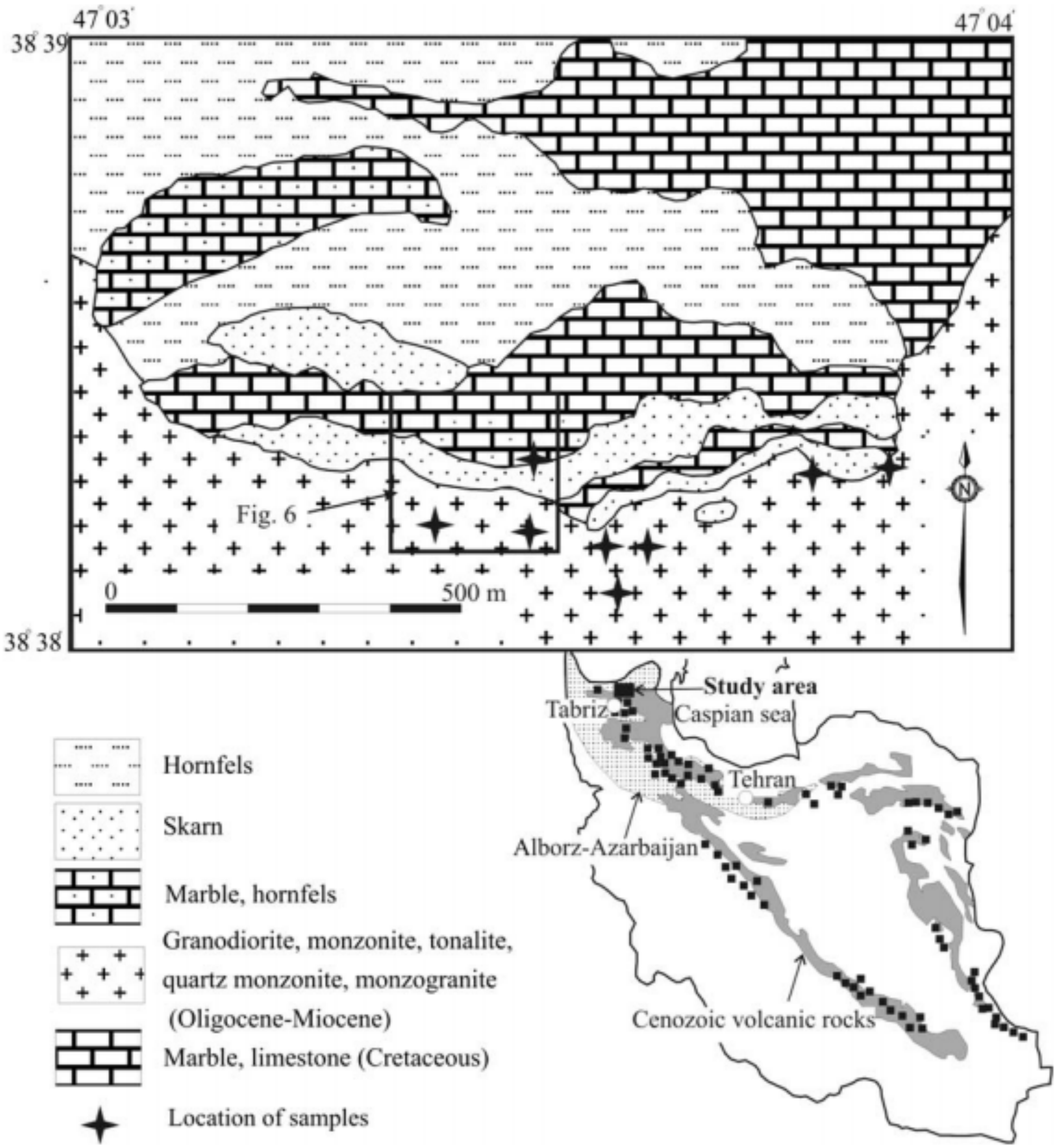

Figure 4: The geological map of the Mazraeh area. The map includes the data of Cenozoic volcanic rocks (Darvishzadeh, 1991) and the batholith belts (Berberian *et al.*, 1982). Plutons are presented by the black squares. Taken from Karimzadeh Somarin (2010).

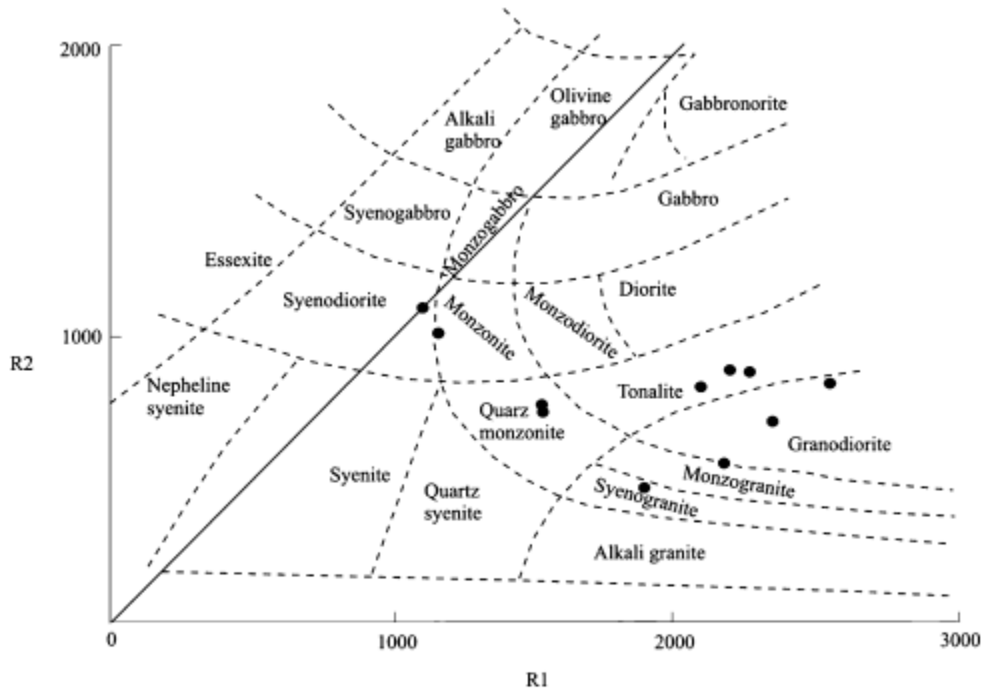

Figure 5: The R1-R2 diagram (De la Roche *et al.*, 1980) that shows the various compositions of the Mazraeh plutons. Taken from Karimzadeh Somarin (2010).

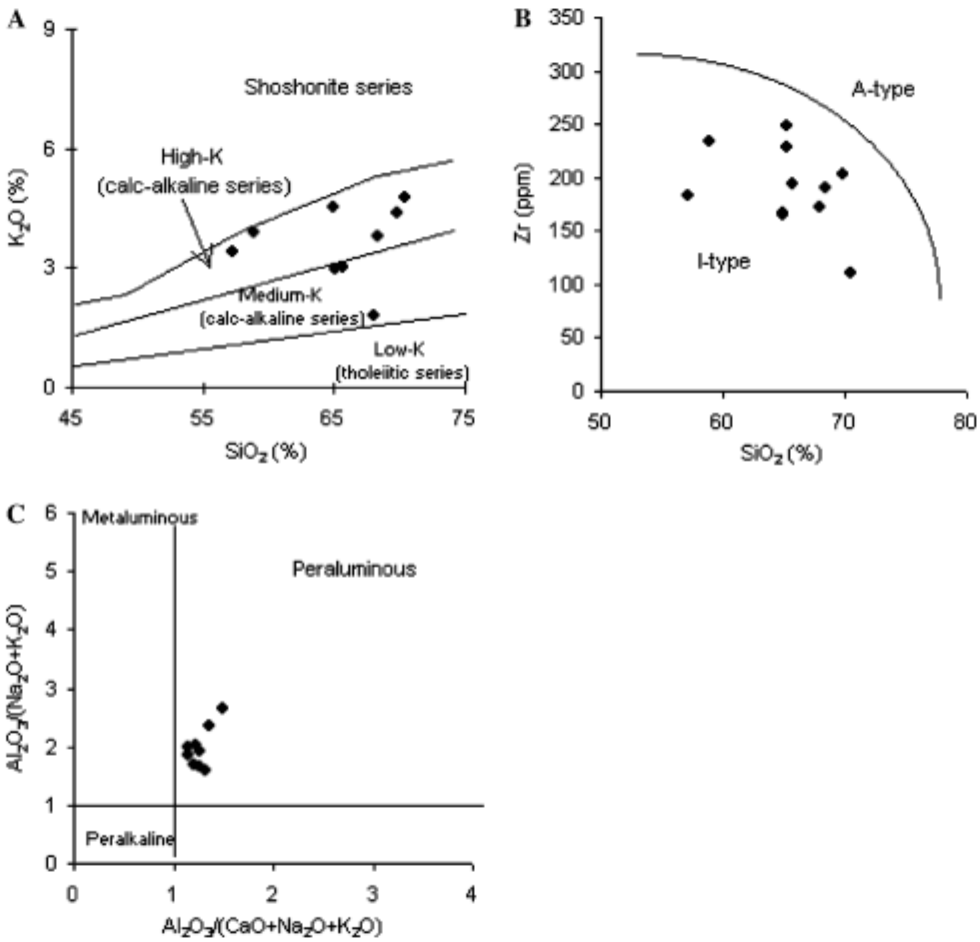

Figure 6: The classification diagrams of the Mazraeh plutonic rocks showing the composition of medium to high K calc-alkaline, I-type, and peraluminous characteristics. Taken from Karimzadeh Somarin (2010).

Cu-Fe skarn deposits in the Edong ore district, Middle–Lower Yangtze River metallogenic belt, China

The Middle-Lower Yangtze River metallogenic belt (MLYRB) is located on the northern margin of the Yangtze Craton, and alongside the North China Craton and Dabieshan orogenic belt (Fig. 7). There are several important faults involved in the formation of the MLYRB. These are the regional strike-slip Tancheng–Lujiang Fault, Xiangfan–Guangji Fault, and Yangxing–Changzhou Fault. A study by Chang *et al.* (1991) provided geochemical evidences, suggesting that the Yangtze fracture zones that exist in the MLYRB were formed due to the development of an extensive network of faults and S-style folds. The trending faults and folds of NE-SW were linked to the subduction of the Pacific Plate (Chang *et al.*, 1991).

There are three major tectono-stratigraphic units that formed the MLYRB: Archean–Proterozoic metamorphic rocks, Cambrian to Early Triassic marine sedimentary rocks, and Middle Triassic to Cretaceous volcanic and terrigenous clastic rocks (Xie *et al.*, 2015). The basement rocks consist of Archean to Middle Proterozoic phyllite, slate, and meta-basalt, interposed with 990-2900 Ma metaspilite and keratophyre (Chang *et al.*, 1991). There is an unconformity of Cretaceous volcanic and volcano-clastic rocks, such as breccia, tuff, andesite, basalt, and rhyolite, overlying the previously-settled sedimentary rocks (Chang *et al.*, 1991).

The Edong ore deposit is located in the western part of the MLYRB (Fig. 7). The metamorphic rocks from the Late Proterozoic are poorly exposed in the southern part of the MLYRB. On the other hand, Cambrian to Middle Triassic marine carbonate and clastic sequences are widespread, and the clastic rocks of the Late Triassic to Middle Jurassic are locally exposed (Shu *et al.*, 1992). There are six major plutons in the Edong ore district (Fig. 7). The details are provided in Table 3. Cu-Fe skarn deposit occurs in the vicinity of the Yangxin pluton. The host rocks involved in this skarn deposit are dolomitic marble and Early Triassic Marble (Xie *et al.*, 2015).

Table 3: The major plutons at the MLYRB with the compositions, the location, and the area for each pluton. Modified from Xie *et al.* (2015).

Name of pluton	Compositions	Location at the MLYRB	Area (km^2)
Echeng	Granite, monzonite, minor quartz diorite	Southwestern	~100
Tieshan	Quartz diorite, minor gabbro	South	~140
Jinshandian	Quartz diorite; diorite	East; West	~16; ~3
Lingxiang	Diorite, quartz diorite	Unspecified	~90
Yinzu	Quartz diorite	Unspecified	~90
Yangxin	Quartz diorite, minor diorite, granite porphyry	Unspecified	~215

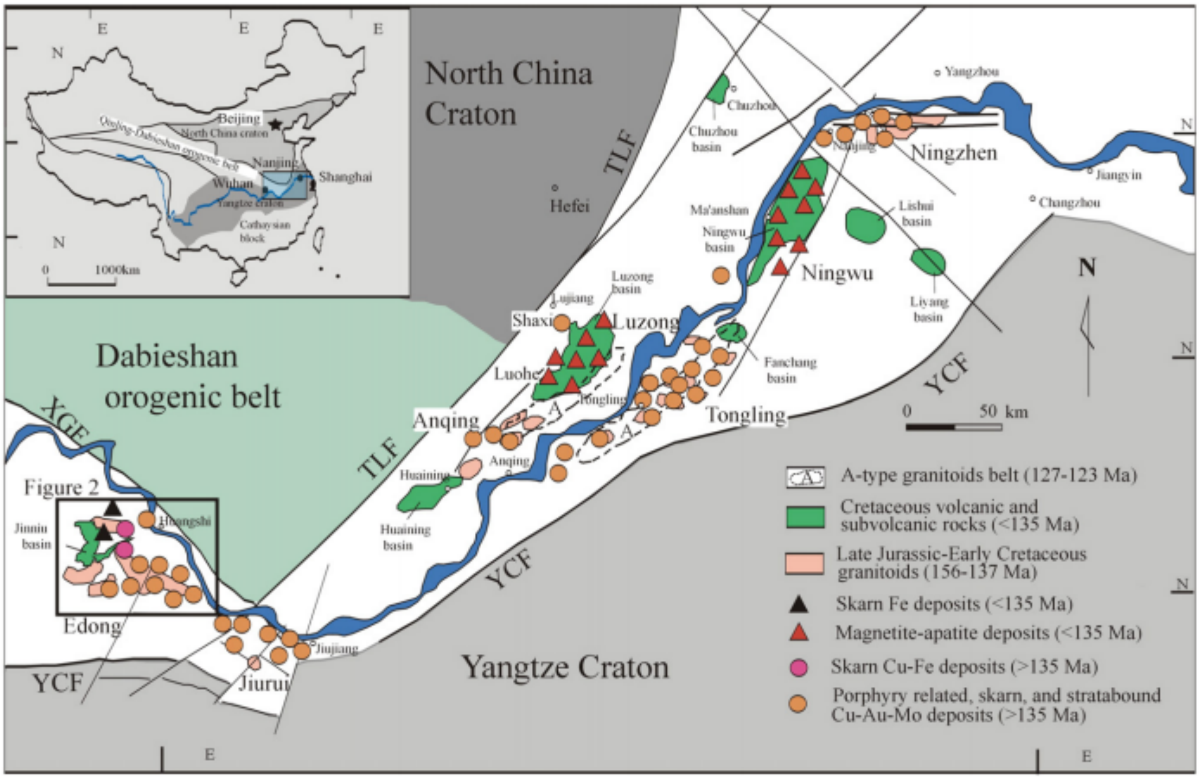

Figure 7: The geological map of the Edong district area, consisting of North China Craton, Dabieshan orogenic belt, and Yangtze Craton. The map also shows the Late Mesozoic granitoids and volcano-sedimentary basins alongside the MLYRB. . TLF: Tancheng–Lujiang Fault, XGF: Xiangfan–Guangji Fault, YCF: Yangxing–Changzhou Fault. Taken from Xie *et al.* (2015).

METHODS

Data Selection

This thesis compares the similarities and the differences in the studies by Xie *et al.* (2015) and by Karimzadeh Somarin (2010) of the copper-iron (Cu-Fe) skarn deposits from the Edong district, China, and the Mazraeh skarn deposit, Iran respectively. This thesis also reviews the data from previous publications and from the Petrological Database (PetDB) concerning the analysis of mineralogy and petrology of skarn deposits and skarn systems from different regions of the world. The data mainly consist of the mineral assemblages, ternary plots, end-member minerals, and thin sections of different types of skarn deposits. The additional data such as geologic and tectonic settings for each type of skarn deposit are also incorporated to further understand the skarn systems and how they develop and evolve in time and space.

Skarn Formation

This thesis studies the formation of the Cu-Fe skarn deposits by using basic questions of five Ws in order to examine the topic in detail. This set of questions is very helpful in determining the processes of skarn formation. The five Ws in this study consist of Who, What, Where, When, and Why, but the Who question is changed to what lithology or rocks are involved to make the question more reasonable for a thesis. Apart from those questions, another question, which is How, is also included to get a more comprehensive information of the skarn formation. The general questions for the skarn formation in this study are listed below:

- Who: What rocks or formations are involved to form skarn? What fluids are involved?
- What: What is a skarn formation? What happens during the skarn formation? What is a skarn deposit?
- Where: Where do skarn deposits form?
- When: When do skarn deposits form?
- Why: Why do skarn deposits form?
- How: How do skarn deposits form?

Skarn Mineralogy

This thesis evaluates and compares the methods used in the previous studies to recognize and define different type of skarn deposits and their economic potentials. This thesis also aims to study the common minerals of skarn deposits and their end-members, thus further comparisons could be made.

One of the modern methods to study mineralogy of skarn deposits is the electron probe micro-analyzer (EPMA). Also known as electron microprobe, this instrument is used to analyze geological materials, for instance skarn deposits *in situ* and to acquire quantitative and precise elemental analysis as little as 1–2μm. Some of the major applications of the EPMA that are important in this study are described below:

- Studying the individual phases of igneous and metamorphic minerals
- Mineralogical analysis of skarn deposits at various scales
- Constructing high resolution images that are useful for the petrological analysis of skarn deposits

After the deposits have been analysed using the EPMA or other instruments, there are various techniques to understand and to describe the variations of skarn deposits using compositional variations of solid-solution series, mineral compatibilities, and the most importantly, mineral phase equilibria to examine mineralogy of different skarn types (Zharikov, 1970). The work of Zharikov (1970) is considered the seminal paper in the study of skarn deposits, and his ideas are extended by Burt (1977, 1982) and Einaudi *et al.* (1981) as compositional variations of common skarn minerals are discussed. Another important instrument is the Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscopy (SEM/EDS). This instrument is an analytical technique used to study the elemental analysis or chemical compositions of skarn minerals (Karimzadeh Somarin, 2010).

This thesis also examines the triangular plots, also known as ternary plots from previous articles that are used to understand the formation of complex minerals such as garnet and pyroxene, the percentages for each mineral tested, and their end-members.

Skarn Petrology

This thesis reviews the analysis of thin sections from previous studies and compares the characteristics of each Cu-Fe skarn deposit. One of the popular techniques to study petrology is by using polarizing microscopes. Polarizing microscopes are used to observe the characteristics and textures of the thin sections for each skarn deposits to determine the nature of various kinds of rocks and minerals under different magnification scales (10x, 50x, and 100x). A polarizing microscope consists of three main parts: the circular stage, the polarizer, and the analyzer. The stage helps to make sure the thin sections analyzed are fixed above it for thin section analysis. The polarizer controls the amount of light passing through it. The analyzer also controls the amount of light, and the light direction to help illuminating the thin sections. The textures are then described and compared to determine their petrogenesis and how they developed over time. Textures that indicate fluid inclusions from thin sections of previous studies would also be analyzed for further interpretation, if applicable. The study of fluid inclusions is important because the analysis can provide essential geological information such as the salinity, temperature, and pressure during the formation of skarn and skarn deposits.

RESULTS

Skarn Mineralogy

Based on the mineral assemblages, the Mazraeh Cu-Fe skarn deposit is classified into three main categories or zones:

1. Garnet skarn: Composed of two major types, which are the red-brown andraditic garnet, typically found in the endoskarn zone, and yellow-green grossular garnet, typically found in the exoskarn zone. The grain size of andraditic garnet is up to 4 cm in size. The textures of hand specimens suggest zoning. The straight boundaries and absence of the replacement textures between the garnet and the clinopyroxene suggest that the two minerals have gone through synchronous mineralization. Both minerals have been replaced by epidote, scapolite, actinolite-tremolite, quartz, and calcite. Sources of copper and iron such as pyrite, magnetite, and chalcopyrite might fill interstitial sites and fractures.
2. Pyroxene skarn: Composed of clinopyroxene (diopside-hedenbergite), garnet which is replaced by quartz, calcite, and magnetite during late stages of hydrothermal activity. Sulfide minerals are absent or rare in this type of skarn.
3. Epidote skarn: Irregular green bodies composed of epidote, chlorite, calcite, quartz, pyrite, chalcopyrite, and magnetite. This type is not found in the endoskarn zone.

Further analysis of the garnet composition using the SEM-EDS shows that the red-brown andraditic garnet consists of 45.08– 68.33 mol% andradite, 19.05–39.34 mol% grossular, and 4.52–12.33 mol% almandine and contains 288-680 ppm Cu. The green-yellow grossular garnet consists of 64.25–78.88 mol% grossular, 8.77– 20.55 mol% andradite, and 7.51–11.49 mol% almandine and contains 17 ppm Cu, a much lower value compared to the andraditic garnet (Karimzadeh Somarin, 2010). The study by Karimzadeh Somarin (2010) proves that the content of copper is higher in the andraditic garnet than the grossular garnet.

As the paper by Karimzadeh Somarin (2010) mostly focuses on garnet, the data for pyroxene are lacking to compare with the Cu-Fe skarn deposit in the Edong ore district. The author mentions that the type of pyroxene is diopside, which is parallel with the review by Meinert (1992). However, the data for garnet composition are more than enough as a proxy for the prograde skarn mineralization to make comparisons with the Cu-Fe and Fe skarn deposits in the Edong ore district, MLYRB, China.

Both endoskarn and exoskarn are well-developed in the Mazraeh Cu-Fe skarn deposits. Exoskarn resulted from the wall-rock interaction of the magmatic hydrothermal fluid and the calcareous wall rock. Since all types of skarn are found in the exoskarn compared to the endoskarn, the exoskarn has been the main site of the Cu mineralization.

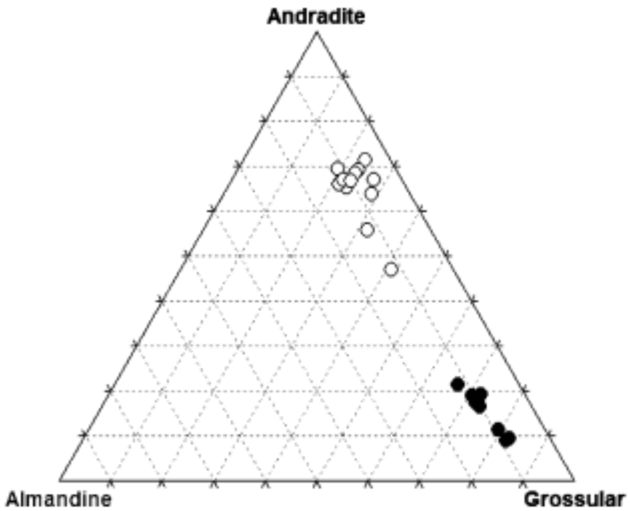

Figure 8: The triangular plot showing compositional variations of garnet of the Mazraeh Cu-Fe skarn deposit. White circles represent endoskarn and black circles represent exoskarn. Taken from Karimzadeh Somarin (2010).

Previous studies have shown that the Cu-Fe skarn deposit in the Edong ore district is characterized by well-developed exoskarn and minor endoskarn adjacent to the contact zones between the Late Mesozoic granitoids and the Triassic sedimentary rocks. The mineralization of Cu and Fe occurs in exoskarns, which are dominantly associated with the pyroxene skarn (Chang et al.,1991; Shu et al., 1992; Zhai et al., 1992; Zhao et al., 1990).

The garnets in the Cu-Fe and Fe skarn deposits are classified into two major types: The first type consists of the early garnet that mainly occurs as patchy aggregates replaced by magnetite. The second type is the late garnet that occurs as veinlets, cutting across the prograde and retrograde skarn minerals. The condition also suggests that the early garnet is associated with the mineralization compared to the late garnet, which is produced post-kinematic. Both the Cu-Fe and Fe skarn deposits have similar garnet and pyroxene compositions. For the Fe skarn deposit, the garnet composition is 37–100 mol% andradite and 0–62 mol% grossular. The pyroxene composition is 61–100 mol% diopside and 0–38 mol% hedenbergite (Figure 9). For the Cu- Fe skarn deposit, the garnet composition is 29–95 mol% andradite and 0–68 mol% grossular. The pyroxene composition is 54–98 mol% diopside and 2–45 mol% hedenbergite (Figure 9).

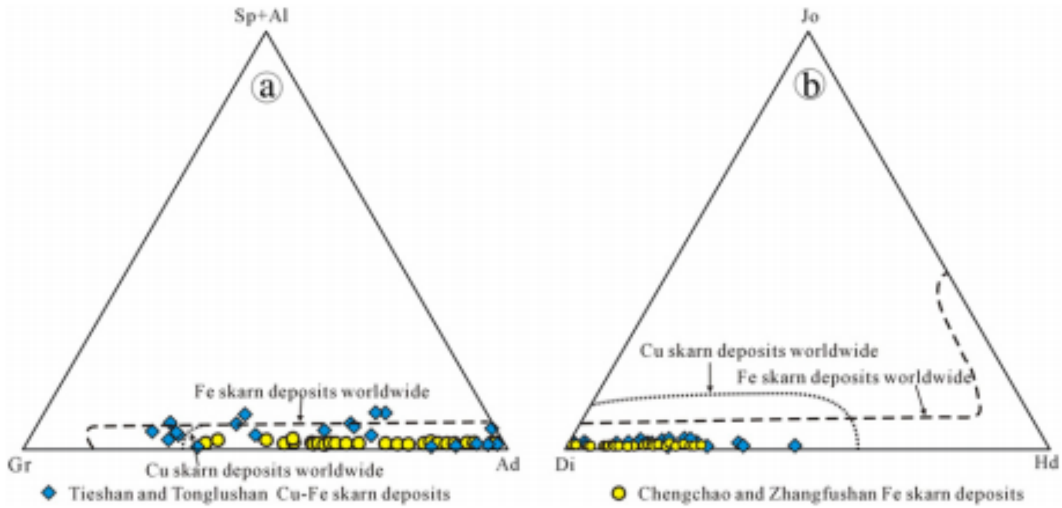

Figure 9: The triangular plots showing compositional variations of (a) garnet and (b) pyroxene of the Cu-Fe and Fe skarn deposits in the Edong ore district, MLYRB. The compositions of garnet and pyroxene for Cu and Fe skarn deposits worldwide are also included. Taken from Xie *et al.* (2015). Ad: andradite, Gr: grossular, Sp: spessartine, Al: almandine, Di: diopside, Hd: hedenbergite, Jo: johannsenite

The Fe and Cu-Fe skarn deposits in the Edong ore district have well-developed exoskarn with minor endoskarn along the contact zones of the Late Mesozoic granitoids and the Triassic sedimentary rocks. Most of the Cu and Fe mineralization occur in the exoskarns, which are typically associated with the pyroxene skarn in the district.

For the two skarn deposits from two different geologic settings, the garnet and pyroxene compositions are relatively similar, although the compositions might change over time under different suitable conditions of temperature and pressure. Therefore, the prograde skarn minerals, such as garnet and pyroxene are not the critical factor in controlling the differences between Cu-Fe skarn deposits from both sites. Both sites also have relatively similar system of exoskarn and endoskarn. The well-developed exoskarn is the main site for Cu and Fe mineralization (Chang et al., 1991; Shu et al., 1992; Zhai et al., 1992; Zhao et al., 1990).

Skarn Petrology

Based on the skarn petrology, the Mazraeh Cu-Fe skarn deposits have textures of prograde skarn minerals such as garnet and pyroxene that are overprinted by retrograde skarn minerals that formed during late stage after the skarn deposit formation (Fig. 10A, D, E). In certain cases, only relict garnet is seen (Fig. 10E). Garnet and pyroxene form during synchronous mineralization indicating that they form at the same time (Fig. 10B).

Chalcopyrite and pyrite formed as rims around the magnetite grain, indicating that magnetite was unstable due to the reaction with its surrounding crystals or melts. Chalcopyrite and pyrite also fill the interstitial sites and fractures, suggesting that they form late-stage of the skarn formation (Fig. 10C).

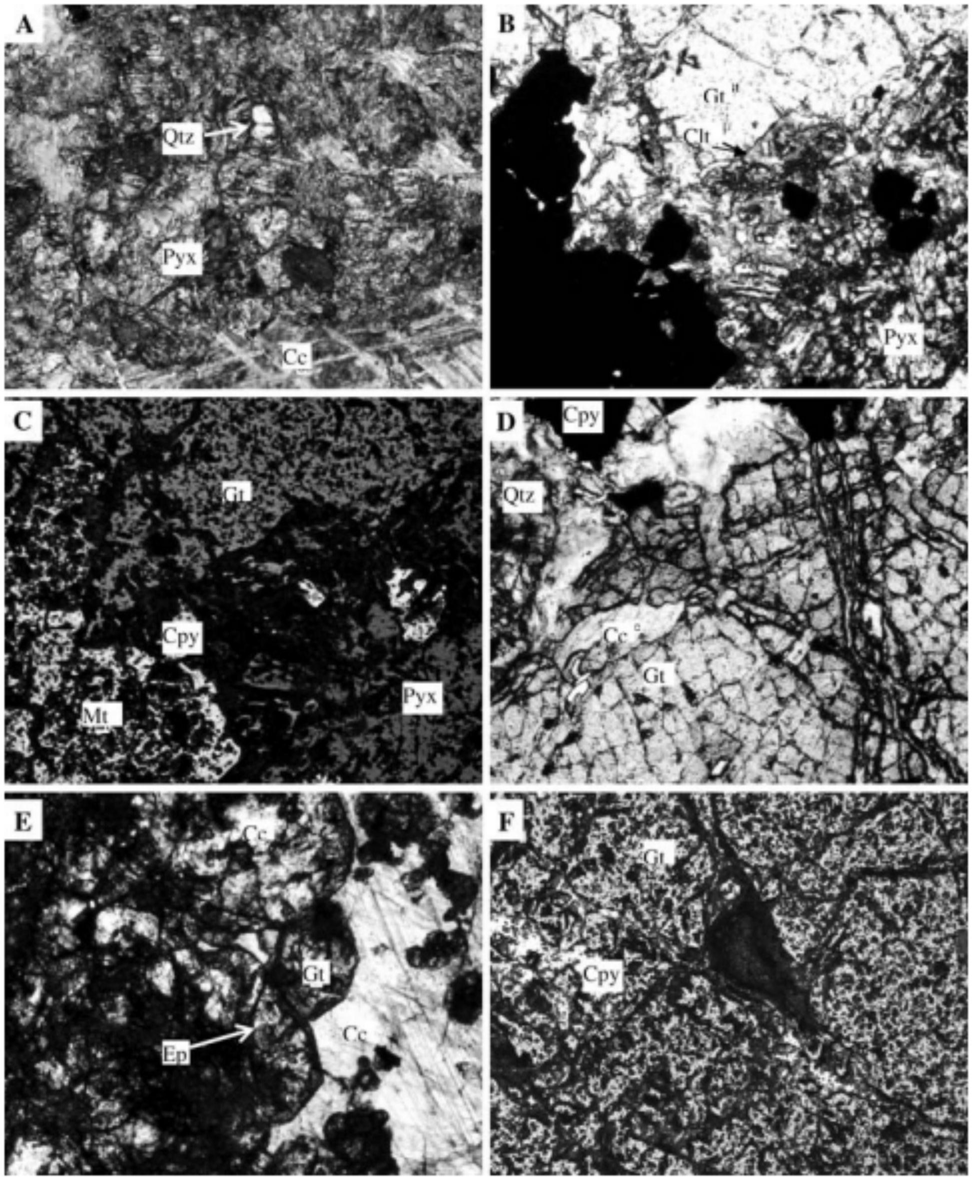

Figure 10: The petrological analysis from the Mazraeh Cu-Fe skarn deposit. A: The pyroxene grains are replaced by calcite and quartz (CPL). B: The straight boundary between garnet and pyroxene. Chlorite is also visible under PPL. C: The rims of chalcopyrite around the magnetite crystal (CPL). D: Fractures that are filled with calcite, quartz, and chalcopyrite in a zoned andraditic garnet (PPL). E: Garnet is being replaced by calcite, epidote, and quartz (CPL). F: Chalcopyrite fill in the fractures in garnet crystal (CPL). CPL: Cross-polarized light, PPL: Plane-polarized light, Pyx: pyroxene, Gt:garnet, Clt: chlorite, Cc: calcite, Cpy: chalcopyrite, Mt: magnetite, Qtz: quartz, Ep: epidote. Taken from Karimzadeh Somarin (2010).

Since no petrological analysis could be found for the Cu-Fe and Fe skarn deposits in the Edong ore district, the adjacent Fe skarn deposits in the Taochong deposit of the MLYRB. There are three main stages established due to the differences in the petrology textures (Table 4).

Table 4: The mineralization stage of the Fe skarn deposits in the Taochong district of the MLYRB. Data are taken from Cao *et al.* (2012).

Mineralization Stage	Characteristics
Skarn	Formation of anhydrous minerals, dominated by garnet and pyroxene. Garnet skarn exhibits the equigranular texture. Garnet skarn is compositionally zoned relative to the individual crystal.
Iron Oxide	Formation of the ore body, dominated by the replacement of garnet and pyroxene by actinolite, calcite, quartz, chlorite, and hematite. The ore minerals include hematite, magnetite, and pyrite.
Carbonate	Formation of calcite veins that crosscut the skarn and the ore body, producing stockwork textures. The formation indicates that they were formed during the declining stage of the hydrothermal system.

The ore minerals are dominated by hematite and magnetite, with minor pyrite. Hematite is the most important ore mineral in the Taochong deposit, and it usually forms as elongated euhedral crystals (Fig. 11B, C).The vugs are filled with the gangue minerals, such as macrocrystalline calcite and relatively small quartz crystals, indicating late-stage alteration of the iron skarn deposit. Textures from the thin sections also suggest that the prograde skarn minerals are replaced by the retrograde skarn minerals, such as quartz, calcite, chlorite, actinolite, and hematite (Fig. 11E, F).

Some similarities are observed in the petrological analysis from the Mazraeh Cu skarn deposit and Taochong Fe skarn deposit:

1. Prograde skarn minerals, for example garnet and pyroxene form in synchronous mineralization.
2. Both skarn deposits have relatively similar textures that indicate replacement of prograde skarn minerals by retrograde skarn minerals, including the ore minerals. For Cu skarn deposit, the most common ore mineral is chalcopyrite. For Fe skarn deposit, the most common ore minerals are hematite and magnetite.
3. The replacement minerals, such as calcite and quartz crosscut the skarn deposits, indicating that the alteration took place after the skarn deposit formation. The minerals typically fill in the interstitial spaces and vugs. In certain cases, the replacement processes create the stockwork veins texture, mainly by calcite.

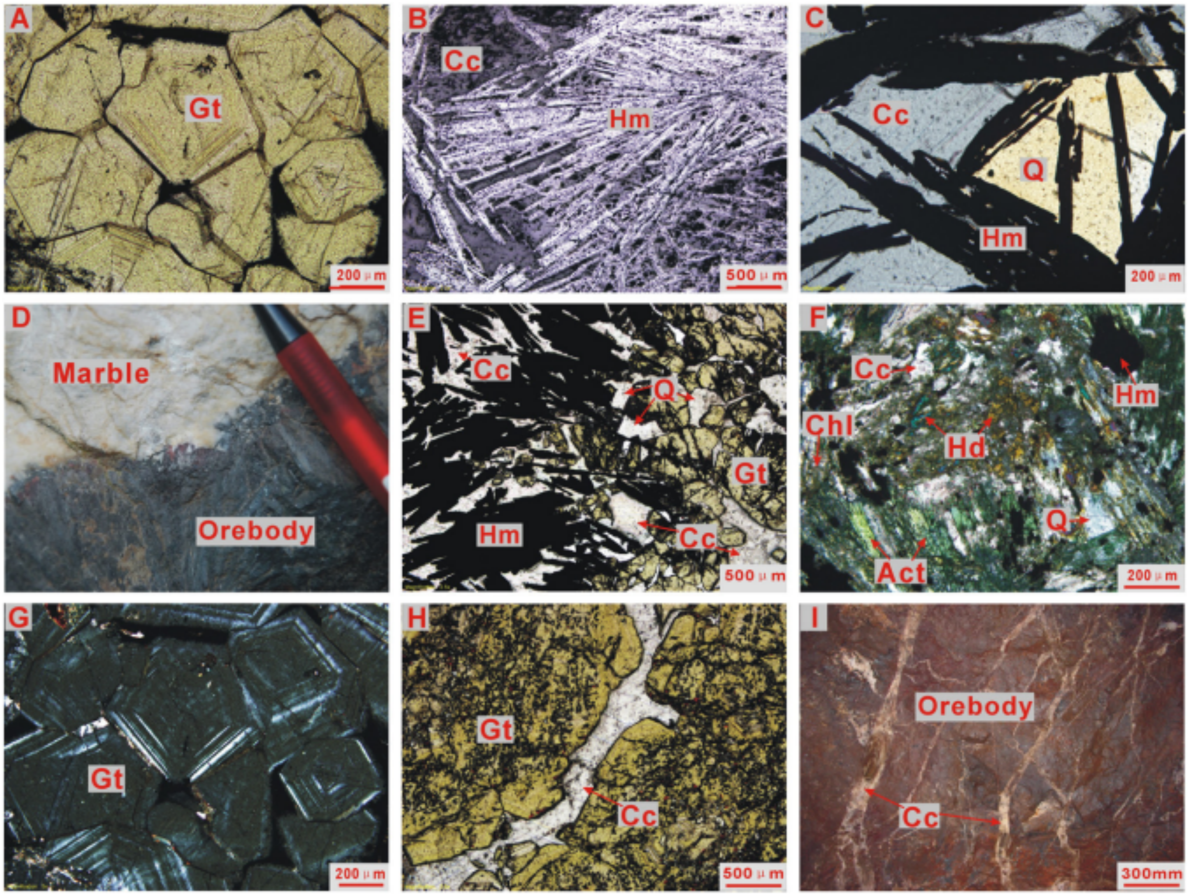

Figure 11: Petrological analysis from the Taochong Fe deposit in the vicinity of the Edong ore district. A: Garnet displays equigranular textures (PPL).B and C: The formation of aggregates of hematite crystals, intergrown with calcite and quartz (PPL for B, CPL for C). D: The contact of marble (carbonate rock) and the orebody. E and F: The garnet and pyroxene are replaced by retrograde minerals such as chlorite, quartz, calcite, hematite, and actinolite. The replacement produces stockwork textures (PPL for E, CPL for F). G: Garnet displays compositional zoning (CPL). H and I: Calcite veins cut across the skarn and the orebody. CPL: Cross-polarized light, PPL: Plane-polarized light, Gt: garnet, Hd: pyroxene, Act: actinolite, Clt: chlorite, Mt: magnetite, Cc: calcite, Qtz: quartz. Taken from Cao *et al.* (2012).

DISCUSSION

Replacements of prograde skarn minerals by retrograde skarn minerals

Published papers on skarn formation and skarn deposits have suggested that the skarn deposits are characterized by a similar progression of prograde towards retrograde skarn minerals, regardless of the skarn types. Various retrograde minerals also start to form retrogressively due to the cooling down of rock. Typically, the prograde garnet and pyroxene are replaced by the retrograde epidote, amphibole, chlorite, and other hydrous minerals that can form in relatively lower temperature and pressure (Meinert *et al.*, 2005). Skarn minerals also might have various calc-silicate minerals, but usually are dominated by the garnet and pyroxene, although the compositional variations might be different. Based on the review by Meinert (1992), the compositions of garnet and pyroxene are relatively similar in different types of skarn deposits classified by the important economic elements.

For the petrology of Mazraeh Cu-Fe skarn deposits and the Cu-Fe skarn deposits in the Edong ore district, the textures created by the retrograde minerals overprinted the textures created by the prograde minerals, proving that the retrograde minerals formed after the formation of prograde skarn minerals. Similar textures are observed from different types of skarn deposit. From an example of W-rich skarn deposit in the Tien Shan Gold Belt, western Uzbekistan, the prograde skarn minerals such as pyroxene are overprinted by the retrograde hydrous minerals such as amphibole, quartz, and chlorite (Fig. 12E). Only the mineral assemblages are different based on the types of skarn deposits (Fig. 12).

Most of the skarns are formed from the hydrothermal fluids of magmatic origin (magmatic fluid) that intrude into the host or country rocks, typically carbonate rocks (Meinert, 1992). The high temperature provided by the magmatic fluid provides suitable conditions for the prograde skarn minerals to form and develop in the host rocks. As the temperature reduces over time, retrograde skarn minerals start to form and develop, creating textures that overprint the textures created by the prograde minerals.

Other than temperature, pressure and salinity provided by the hydrothermal fluid are also important in the skarn formation. Pressure has effects similar to those of temperature on the formation of skarn minerals. Typically, prograde skarn minerals form in high pressure, while retrograde skarn minerals form in lower pressure. When the pressure starts to decrease in the skarn deposit, the retrograde minerals, including the typical secondary alteration minerals, such as quartz and calcite, might start to form and fill in the fractures and joints in the deposit. Hydrothermal fluids with high salinity contain higher concentration of the ions, hence transporting more ions during the intrusion process. However, other factors such as the type of hydrothermal fluid and the type of host rock should also be taken into considerations. Thus, if optimum conditions are provided to form skarn minerals, the general outcome would be that the prograde and retrograde minerals would form faster due to the availability of ions provided by the high salinity hydrothermal fluids.

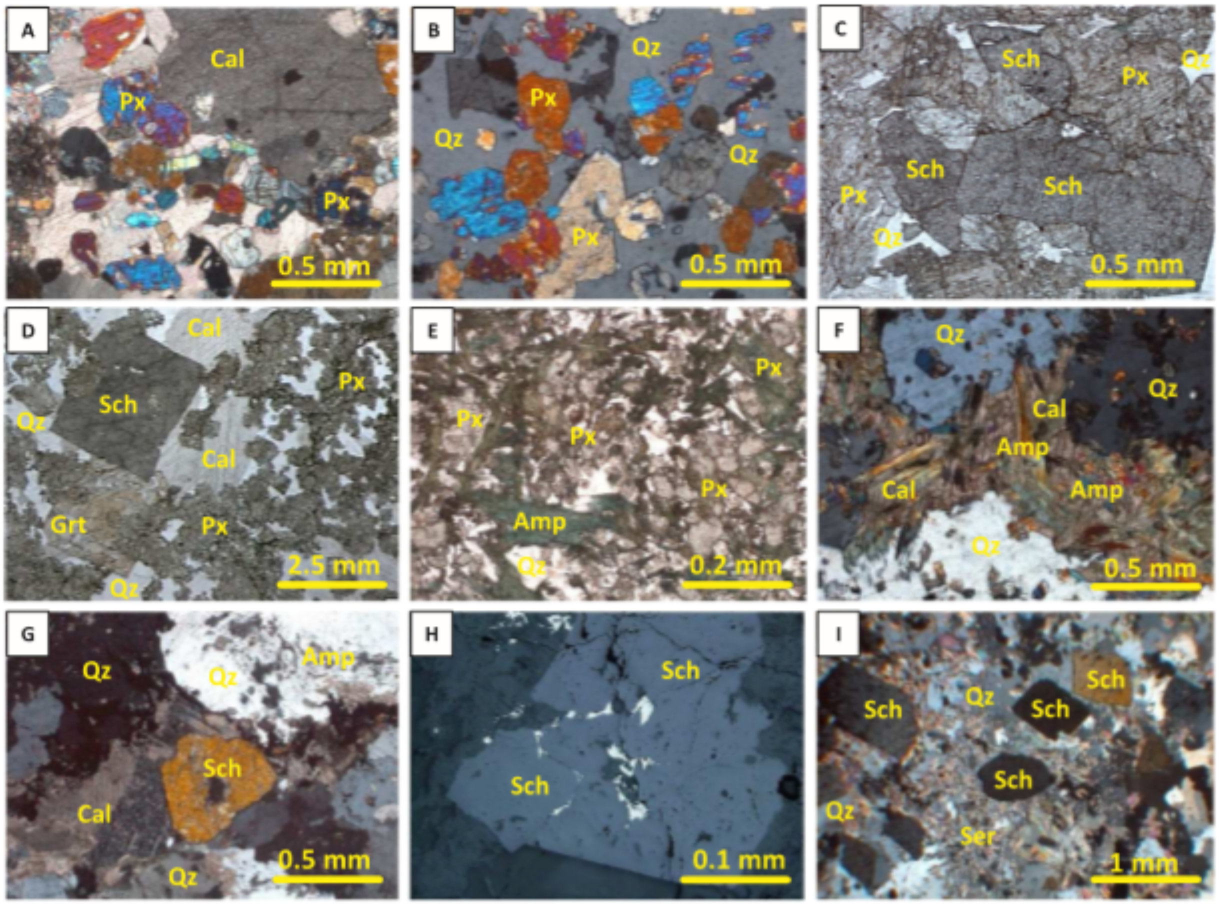

Figure 12: The petrological analysis of the W-rich skarn deposit in the Tien Shan Gold Belt, western Uzbekistan. A: pyroxene skarn replacing coarse-grained calcite marble (CPL). B: recrystallized pyroxene tends to become euhedral (CPL). C, D: Scheelite in pyroxene-quartz skarn. E: Amphibole-quartz-calcite (propylitic) overprints the pyroxene skarn. F: alteration of amphibole-quartz-calcite (propylitic). G: Scheelite in amphibole-quartz-calcite (propylitic). H: Inclusion of scheelite in amphibole-quartz-calcite (propylitic). I: Scheelite in quartz-albite-carbonate-sericite (phyllic). CPL - Cross-polarized light, Grt – garnet, Qz – quartz, Cal – calcite, Px – pyroxene, Sch – scheelite, Amp – amphibole, Ser – sericite. Taken from Soloviev and Kryazhev (2018).

Type of garnet and pyroxene

The Mazraeh Cu-Fe skarn deposits and the Cu-Fe skarn deposits have the same dominant types of garnet, which is andradite and of pyroxene, which is diopside. Andradite is also known as the Fe-rich garnet based on its chemical composition. Andradite is favorable in the Cu-Fe skarn deposits because of the availability of Fe ions mainly from the magmatic fluid that significantly helps to form andradite compared to other types of garnet.

Meanwhile, for pyroxene type, diopside is expected to have Cu and Fe ions in its chemical composition because the Cu-Fe skarn deposit contains high amount of Cu and Fe ions. However, the chemical composition of diopside is $CaMgSi_2O_6$ and forms a series with hedenbergite, which is the Fe-rich end member of diopside. Cu-Fe skarn deposit should a have higher percentage of hedenbergite than diopside because the chemical composition of hedenbergite is $CaFeSi_2O_6$ that contains Fe ions. The main reason for diopside formation might be because of the type of host rock for each Cu-Fe skarn deposit.

The host rock of the Cu-Fe skarn deposit in the Edong ore district is dolomitic marble, which contains Mg. The concentration of Mg in the dolomitic marble might be favorable towards the formation of diopside, instead of hedenbergite. On the other hand, the host rock of the Mazraeh Cu-Fe skarn deposit is limestone. The formation of diopside instead of hedenbergite might be because the Fe ions provided from the intrusion of hydrothermal fluid into the host rocks are not widespread and might be contained. Hence, both diopside and hedenbergite can be found in this skarn deposit.

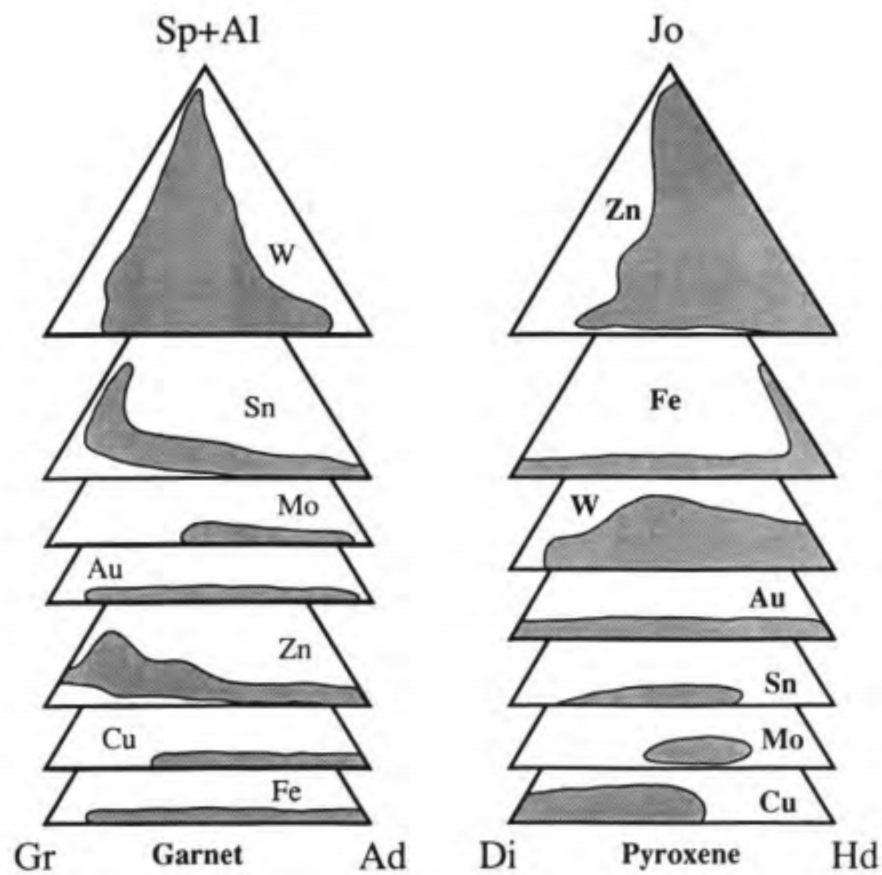

Figure 13: The ternary plots of garnet and pyroxene for different types of skarn deposit based on the important economic elements. For garnet, andradite is dominant in the Cu and Fe skarn deposit. For pyroxene, diopside is dominant in the Cu skarn deposit. Fe skarn deposit has both diopside and hedenbergite. The types of garnet and pyroxene for the Cu-Fe skarn deposit are expected to be in between of the types Cu and Fe skarn deposits would have. Taken from Meinert (1992).

CONCLUSIONS

There are more similarities than differences between the Mazraeh Cu-Fe skarn deposit and the Cu-Fe skarn deposit in the Edong ore district based on the mineralogical and petrological analysis from the two deposits. In summary:

1. Both deposits have well-developed exoskarn and endoskarn system. The exoskarn contains more Cu and Fe mineralization due to the more suitable conditions, including temperature and pressure compared to endoskarn. The hydrothermal fluids came from the magmatic source.
2. The prograde skarn minerals are not the controlling factor to differentiate the two deposits. Both Cu-Fe skarn deposits share relatively similar compositions of garnet and pyroxene. For the Mazraeh Cu-Fe skarn deposit, the endoskarn contains the red-brown andradite with composition of 45.08– 68.33 mol% andradite, 19.05–39.34 mol% grossular, and 4.52–12.33 mol% almandine. The exoskarn contains the green-yellow grossular garnet consists of 64.25–78.88 mol% grossular, 8.77– 20.55 mol% andradite, and 7.51–11.49 mol% almandine. The pyroxene is diopside-rich. The Cu-Fe skarn deposit in the Edong ore district contains 29–95 mol% andradite and 0–68 mol% grossular. The pyroxene is also diopside rich with 54–98 mol% diopside and 2–45 mol% hedenbergite.
3. Petrological analyses for both deposits suggest that the garnet and pyroxene form during synchronous mineralization. The prograde minerals are replaced by the retrograde minerals, including the ore minerals that provide the sources for Cu and Fe. Important ore minerals in the Cu-Fe skarn type are pyrite, hematite, and chalcopyrite. Other retrograde minerals such as calcite and chlorite fill in the interstitial spaces and vugs, and may create stockwork veins texture.

Recommendations for Future Work

There are many exhaustive reviews regarding the skarn deposits based on the important economic elements, but the relationships of skarn deposits that contain more than one economic elements, such as Cu-Fe are poorly explained. Mineralogy and petrology are two important aspects that are significant in studying and understanding various metasomatic processes that form skarn deposits. The constructions of the ternary plots with the end-members are also vital to compare the characteristics of skarn deposits in different places.

Other than mineralogy and petrology, there are many aspects to study the skarn formation and the skarn deposits in detail, such as fluid inclusion petrography and stable isotope studies. These are needed to examine fully the characteristics for each type of skarn deposit classified based on the economic elements. The studies mentioned are also applicable towards understanding the formation of other metasomatic and metamorphic rocks.

References Cited

Berberian, F., Muir, I. D., Pankhurst, R. J., & Berberian, M., 1982, Late Cretaceous and early Miocene andean-type plutonic activity in northern Makran and central Iran. Journal of the Geological Society of London, 139, Part 5, 605–614.

Billingsley, P. and Hume. C.B., 1941, The ore deposits of Nickel Plate Mountain, Hedley, B.C.: Canadian Institute of Mining and Metallurgy, Bulletin, v. 44, p. 524-590.

Brooks, J. W., Meinert, L. D., Kuyper, B. A., & Lane, M. L., 1991, Petrology and geochemistry of the McCoy gold skarn, Lander County, Nevada. United States: Geological Society of Nevada : Reno, NV, United States.

Burt, D. M., 1977, Mineralogy and petrology of skarn deposits. Rendiconti Della Societa Italiana Di Mineralogia e Petrologia, 33(2), 859–873.

Burt, D. M., 1982, Skarn deposits; historical bibliography through 1970. Economic Geology and the Bulletin of the Society of Economic Geologists, 77(4), 755–763.

Cao, Y., Du, Y., Gao, F., Hu, L., Xin, F., & Pang, Z., 2012, Origin and evolution of hydrothermal fluids in the Taochong iron deposit, Middle–Lower Yangtze Valley, Eastern China: Evidence from microthermometric and stable isotope analyses of fluid inclusions. Ore Geology Reviews, 48, 225–238.

Chang, Y.F., Liu, X.P., Wu, Y.C., 1991. The Copper–iron Belt of the Lower and Middle Reaches of the Changjiang River (in Chinese). Geological Publishing House, Beijing. 379 pp. (in Chinese with English abstract).

Darling, R. S., 1990, Wide range of molybdenite stability reflected in vein assemblages at the carbonate-hosted Cannivan Gulch stockwork molybdenum deposit, Southwest Montana. Abstracts with Programs - Geological Society of America, 22(7), 180–181.

Darvishzadeh, A., 1991, Geology of Iran. Neda Publication, Tehran, pp 1–901.

Dawson, G. L., & Ray, G. E., 1994, The geology and mineral deposits of the Hedley gold skarn district, southern British Columbia. Bulletin - Ministry of Energy, Mines and Petroleum Resources.

De la Roche, H., Leterrier, J., Grandclaude, P., & Marchal, M., 1980, A classification of volcanic and plutonic rocks using R (sub 1) R (sub 2) -diagram and major-element analyses; its relationships with current nomenclature. Chemical Geology, 29(3–4), 183–210.

Dick, L. A., & Hodgson, C. J., 1982, The MacTung W-Cu(Zn) contact metasomatic and related deposits of the northeastern Canadian Cordillera. Economic Geology and the Bulletin of the Society of Economic Geologists, 77(4), 845–867.

Dobson, D. C., 1982, Geology and alteration of the Lost River tin-tungsten-fluorine deposit, Alaska. Economic Geology and the Bulletin of the Society of Economic Geologists, 77(4), 1033–1052.

Dyer, B., Lee, C.-T. A., Leeman, W. P., & Tice, M., 2011, Open-system behavior during pluton-wall-rock interaction as constrained from a study of endoskarns in the Sierra Nevada Batholith, California. Journal of Petrology, 52(10), 1987–2008.

Einaudi, M. T., & Burt, D. M., 1982, Introduction; terminology, classification, and composition of skarn deposits. Economic Geology and the Bulletin of the Society of Economic Geologists, 77(4), 745–754.

Eineudi, M.T., Meinert. L.D. and Newberry, R.J., 1981, Skarn deposits. Economic Geology, 75th Anniversary Volume, p. 317-391.

Ettlinger, A. D., & Ray, G. E., 1993, Endoskarn and exoskarn formation in the Nickel Plate gold deposit; a give and take relationship. Abstracts with Programs - Geological Society of America, 25(5), 35–36.

Ettlinger, A. D., 1990, Skarn evolution and hydrothermal fluid charateristics in the Nickel Plate Deposit, Hedley, B.C. Program with Abstracts - Geological Association of Canada; Mineralogical Association of Canada: Joint Annual Meeting, 15, 37.

Gaspar, M., Knaack, C., Meinert, L. D., & Moretti, R., 2008, REE in skarn systems; a LA-ICP-MS study of garnets from the Crown Jewel gold deposit. Geochimica et Cosmochimica Acta, 72(1), 185–205.

Hall, D. L., Cohen, L. H., & Schiffman, P., 1988, Hydrothermal alteration associated with the Iron Hat iron skarn deposit, eastern Mojave Desert, San Bernardino County, California. Economic Geology and the Bulletin of the Society of Economic Geologists, 83(3), 568–587.

Hickey, R. J., III., 1990, The geology of the Buckhorn Mountain gold skarn, Okanogan County, Washington. United States.

Hickey, R. J., III., 1992, The Buckhorn Mountain (Crown Jewel) gold skarn deposit, Okanogan County, Washington. Economic Geology and the Bulletin of the Society of Economic Geologists, 87(1), 125–141.

Hou Tong, Zhang Zhaochong, Santosh, M., Encarnacion, J., Zhu Jiang, & Luo Wenjuan., 2014, Geochronology and geochemistry of submarine volcanic rocks in the Yamansu iron deposit, eastern Tianshan Mountains, NW China; constraints on the metallogenesis. Ore Geology Reviews, 56, 487–502.

Jamtveit, B., 1991, Oscillatory zonation patterns in hydrothermal grossular-andradite garnet; nonlinear dynamics in regions of immiscibility. American Mineralogist, 76(7–8), 1319–1327.

Karimzadeh Somarin, A., 2004, Garnet composition as an indicator of Cu mineralization; evidence from skarn deposits of NW Iran. Journal of Geochemical Exploration, 81(1–3), 47–57.

Karimzadeh Somarin, A., 2005, Petrology and geochemistry of Early Tertiary volcanism of the Mendejin area, Iran, and implications for magma genesis and tectonomagmatic setting. Geodin Acta, 18, 343–362.

Karimzadeh Somarin, A., 2006, Geology and geochemistry of the Mendejin plutonic rocks, Mianeh, Iran. Journal of Asian Earth Science, 27, 819–834.

Karimzadeh Somarin, A., 2010, Garnetization as a ground preparation process for copper mineralization; evidence from the Mazraeh skarn deposit, Iran. International Journal of Earth Sciences = Geologische Rundschau, 99(2), 343–356.

Kotlyar, B. B., & Theodore, T. G., 1998, Multilevel geochemical patterns at the Fortitude gold skarn, Battle Mountain mining district, Nevada. Open-File Report - U. S. Geological Survey, 259–263.

Kwak, T. A. P., 1987, W-Sn skarn deposits and related metamorphic skarns and granitoids. Developments in Economic Geology, 24.

Megaw, P. K. M., Barton, M. D., & Graf, A., 1998, Polyphase skarn mineralization associated with a polyphase differentiated composite intrusion, San Martin-Sabinas District, Zacatecas, Mexico. Program with Abstracts - Geological Association of Canada; Mineralogical Association of Canada: Joint Annual Meeting, 23, 122.

Megaw, P. K. M., Ruiz, J., & Titley, S. R., 1988, High-temperature, carbonate-hosted Ag-Pb-Zn(Cu) deposits of northern Mexico. Economic Geology and the Bulletin of the Society of Economic Geologists, 83(8), 1856–1885.

Meinert, L. D., 1992, Skarns and skarn deposits. Geoscience Canada, 19(4), 145–162.

Meinert, L. D., 1993, Igneous petrogenesis and skarn deposits. Special Paper - Geological Association of Canada, 40, 569–583.

Meinert, L. D., Dipple, G. M., & Nicolescu, S., 2005, World skarn deposits. In: Hedenquist, J.W., Thompson, J.F.H., Goldfarb R.J., Richards, J.P., Eds., Economic geology 100th anniversary volume. Society of Economic Geologists, Littleton, v. 1905-2005, 299–336.

Meinert, L. D., Hefton, K. K., Mayes, D., & Tasiran, I., 1997, Geology, zonation, and fluid evolution of the Big Gossan Cu-Au skarn deposit, Ertsberg District, Irian Jaya. Economic Geology and the Bulletin of the Society of Economic Geologists, 92(5), 509–534.

Newberry, R. J., 1983, The formation of subcalcic garnet in scheelite-bearing skarns. The Canadian Mineralogist, 21, Part 3, 529–544.

Newberry, R. J., and Einaudi. M. T., 1981, Tectonic and geochemical setting of tungsten skarn minerallzation in the Cordillera. Arizona Geological Society, Digest, v. 14, p. 99-112.

Newberry, R. J., 1998, W- and Sn-skarn deposits. Mineralogical Association of Canada Short Course Series, 26, 289-335.

Purtov, V. K., Kholodnov, V. V., Anfilogov, V. N., & Nechkin, G. S., 1989, The role of chlorine in the formation of magnetite skarns. International Geology Review, 31, 63–71.

Putnis, A., 2002, Mineral replacement reactions; from macroscopic observations to microscopic mechanisms. Mineralogical Magazine, 66(5), 689–708.

Putnis, C. V., Austrheim, H., Engvik, A. K., & Putnis, A., 2008, A mechanism of fluid infiltration through minerals; implications for element mobilisation within the Earth. Publication Series - Australasian Institute of Mining and Metallurgy, 8/2008, 625–629.

Ray, G. E., Dawson, G. L., & Simpson, R., 1987, The geology and controls of skarn mineralization in the Hedley gold camp, southern British Columbia (92H/8, 82E/5). Paper - Ministry of Energy, Mines and Petroleum Resources, 65–79.

Ray, G. E., Dawson, G. L., & Simpson, R., 1988, Geology, geochemistry and metallogenic zoning in the Hedley gold-skarn camp (92H/08; 82E/05). Paper - Ministry of Energy, Mines and Petroleum Resources, 59–80.

Sangster, D. F., 1969, The contact metasomatic magnetite deposits of southwestern British Columbia. Geological Survey of Canada, Bulletin 172, 79.

Shu, Q. A., Chen, P. L., Cheng, J. R., 1992, Geology of Iron–Copper Deposits in Eastern Hubei Province. Metallurgic Industry Press, Beijing, China, (in Chinese).

Soloviev, S. G., & Kryazhev, S. G., 2018, Tungsten mineralization in the Tien Shan Gold Belt: Geology, petrology, fluid inclusion, and stable isotope study of the Ingichke reduced tungsten skarn deposit, western Uzbekistan. Ore Geology Reviews, 101, 700–724.

Xie, G., Mao, J., Zhu, Q., Yao, L., Li, Y., Li, W., & Zhao, H., 2015, Geochemical constraints on Cu–Fe and Fe skarn deposits in the Edong district, Middle–Lower Yangtze River metallogenic belt, China. Ore Geology Reviews, 64, 425–444.

Zhai, Y. S., Yao, S. Z., Lin, X. D., Zhou, X. N., Wan, T. F., Jin, F. Q., Zhou, Z. G., 1992, Fe–Cu (Au) Metallogeny of the Middle–Lower Changjiang Region. Geological Publishing House, Beijing. 235 pp. (in Chinese with English abstract).

Zhao, Y. M., Lin, W. W., Bi, C. S., Li, D. X., & Jiang, C. J., 1990, Skarn Deposits of China. Geological Publishing House, Beijing, (in Chinese with English abstract).

Zharikov, V. A., 1970, Skarns (part I). International Geology Review, 12(5), 541–559.